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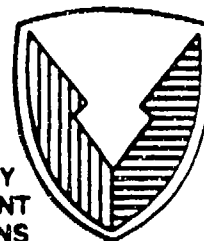
**CHROMATOGRAPHIC SEPARATION METHOD
FOR THE SIMULANT MIXTURE
OF TRIISOPROPYL PHOSPHITE AND
BIS(2-ETHYLHEXYL) HYDROGEN PHOSPHITE**

**Patrick C. Mitchell
Michael W. Ellzy
L. Gail Janes
Irwin Master
Linda L. Szafraniec
William T. Beaudry**

RESEARCH DIRECTORATE

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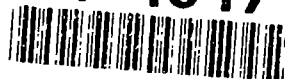
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PREFACE

The work described in this report was authorized under Project No. QPJM05400 and in conjunction with the Bigeye Fill-Close Facility. This work was started in March 1989 and completed in May 1989. The experimental data are contained in laboratory notebooks 88-0126 and 89-0041.

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This report has been approved for release to the public.

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CHROMATOGRAPHIC SEPARATION METHOD FOR THE SIMULANT MIXTURE
OF TRIISOPROPYL PHOSPHITE AND
BIS(2-ETHYLHEXYL) HYDROGEN PHOSPHITE

1. INTRODUCTION

A simulant mixture has been devised for the Bigeye Fill-Close Facility. The ability to analyze for the proposed simulant mixture has called upon an assay analysis for purity. The purity evaluation of triisopropyl phosphite (TIP), bis-(2-ethylhexyl) hydrogen phosphite (BIS), and mixtures of these two compounds is to be performed with gas chromatographic (GC) separation using thermal conductivity detection (TCD). A natural impurity within the TIP is that of diisopropyl hydrogen phosphite (DIP) that could yield an error in the purity results if coelution with TIP occurs.

The DIP component is a source of potential error if it is not completely separated from the TIP. The purpose of this investigation is to perform the initial GC development measures needed for an adequate separation of the three components and to determine a set of operating parameters that can be used for the purity analyses related to TIP, BIS, and TIP/BIS mixtures.

2. CHEMICALS

The three chemicals (and their structures) involved [in-house samples obtained from Ronald J. Piffath, Research Directorate, U.S. Army Chemical Research, Development and Engineering Center, (CRDEC)] in this evaluation follow:

TIP	$[(CH_3)_2CHO]_3P$
BIS	$[CH_3CH_2CH_2CH_2CH(CH_2CH_3)CH_2O]_2P(O)H$
DIP	$[(CH_3)_2CHO]_2P(O)H$

3. PROCEDURE

Using a glovebox, investigators transferred samples of TIP, BIS, and DIP to sample vials under a nitrogen blanket. Additional samples were transferred to tubes in a similar manner for evaluation by Fourier Transform (FT) NMR. The primary method of evaluation was to make individual injections of these chemicals, along with mixture injections of TIP/DIP and TIP/BIS to obtain suitable chromatographic separations of the components. The methods' development involved evaluating instrumental parameters using megabore GC columns.

Initial work involved a Varian model 3400 GC using a flame ionization detector (FID) and a Varian model 3300 GC with a TCD. All columns tested were obtained from J&W Scientific (Rancho Cordova, CA).

3.1 Chromatographic Columns Tested.

The following chromatographic columns were tested:

- 5% phenyl 95% methyl polysiloxane (DB-5) 30 m by 0.54 mm i.d. film thickness: 1.5 μ m
- 100% methyl polysiloxane (DB-1) 15 m by 0.52 mm i.d. film thickness: 1.5 μ m
- 50% phenyl 50% methyl polysiloxane (DB-17) 30 m by 0.54 mm i.d. film thickness: 1.0 μ m
- 14% cyanopropylphenyl 86% methyl polysiloxane (DB-1701) 30 m by 0.54 mm i.d. film thickness: 1.0 μ m

3.2 Varian 3300 Instrumental Parameters.

The parameters for the Varian model 3300 GC follow:

Injection temperature	250 °C
Detector temperature	300 °C
TCD filament temperature	350 °C
Initial column temperature	110 °C
Initial hold time	6 min
Programmed rate	10 °C/min
Final column temperature	250 °C
Final hold time	3 min
Program run time	23 min
Carrier gas	helium
Carrier flow rate	ca. 5 mL/min
Carrier makeup	ca. 30 mL/min

3.3 Purity Determination of Standard Analytical Reference Material Samples by NMR Spectroscopy.

The following segment was provided by the Physical Organic Branch [Chemical Division, Research Directorate, U.S. Army Chemical Research, Development and Engineering Center (CRDEC)].*

*The segment is being used exactly as written by its originator and does not follow standard CRDEC format rules.

NMR Characterization.

General.

Each sample was placed into a clean, dry 5mm O.D. Pyrex NMR tube. The tube was capped with a pressure cap, and the top of the tube wrapped with Parafilm. Multinuclear NMR spectra were run of each sample. For each sample and for each nucleus, the entire chemical shift range for that nucleus was scanned at high amplitude so that all impurities would be detected.

Instrumentation.

The ^1H NMR spectra were recorded using a Varian EM-390 NMR spectrometer operating at 90 MHz. Spectra were recorded at probe temperature (ca. 34C), and quantitative data were obtained by electronic integration of peak areas.

The ^{13}C and ^{31}P NMR spectra were recorded using either a Varian XL-200 Multinuclear NMR System operating at 50 MHz for ^{13}C observation and 81 MHz for ^{31}P observation or a Varian VXR-400S Multinuclear NMR Spectrometer operating at 100 MHz for ^{13}C observation and 160 MHz for ^{31}P observation.

^{13}C Spectra: Spectra were obtained at probe temperature (ca. 20C, VXR-400S; ca. 21C, XL-200), and tetramethylsilane (TMS)/chloroform (CHCl_3) was used as the external reference. For each sample analyzed, at least 250 transients were accumulated using a pulse width of ca. 35 degrees, a sweep width of at least 240 ppm, an acquisition time of at least 1.0 sec, and a pulse delay of at least 2.5 sec. Full proton noise decoupling was used, and "quantitative" data were obtained by digital integration of the peak areas.

^{31}P Spectra: Spectra were obtained at probe temperature (see above), and phosphoric acid (85%) was used as the external reference. For each sample analyzed, at least 64 transients were accumulated using a pulse width of ca. 35 degrees, a sweep width of at least 246 ppm, an acquisition time of at least 0.8 sec and a pulse delay of at least 2.5 sec. In addition, gated proton noise decoupling was used to eliminate any effects from Nuclear Overhauser Enhancement (NOE). Quantitative data were obtained by digital integration of the peak areas.

NOTE: All ^{13}C and ^{31}P spectra were recorded using double precision.

Treatment of data.

All spectra were recorded so that impurities at the 0.5-mole % level could be detected. The overall mole % purity for each sample was calculated using the information from all

spectra recorded for that sample. At least two nuclei were examined for each compound analyzed. After the initial purity determination, re-analyses were conducted by repeating the spectrum from one nucleus for comparison with the original data set. Identification of the impurities present was made, where possible.

Detection Limits: dependent on the field strength of the instrument used to evaluate the sample, the accumulation time for the FT experiment, the nucleus observed and the diameter of the NMR tube.

Examples:

^{31}P ; 81 MHz; 5mm NMR tube; 20 min accumulation time;
Impurities of 0.02 mole % or greater will be detected.

^{31}P ; 32 MHz; 8mm NMR tube; 10 min accumulation time;
Impurities of 0.3 mole % or greater will be detected.

^{13}C ; 50 MHz; 5mm NMR tube; 60 min accumulation time;
Impurities of 0.5 mole % or greater will be detected.

Interferences: any compound or compounds that have the same frequencies (i.e., chemical shifts) as the compounds being evaluated.

4. RESULTS

4.1 NMR Results.

The resulting data obtained from the NMR runs, in conjunction with the GC chromatograms, was used to correlate a separation sequence between the three major components of interest, namely TIP, DIP, and BIS. The results of the NMR evaluations are listed in Table 1. This information was useful in identifying other potential impurities that could result during purity evaluations of TIP and BIS and thus identify the source of contaminant input, where applicable.

4.2 GC Results.

Analysis of the DB-1, DB-5, DB-1701, and DB-17 GC columns resulted in the conclusion that all four columns could effectively separate the TIP and BIS components within a sample mixture. A problem associated with the effective separation of the DIP from the TIP was observed for the more nonpolar columns, DB-1 and DB-5. Chromatographic separations using the DB-1 and DB-5 columns resulted in TIP and DIP overlapping. This coelutive behavior was observed, even at extended initial isothermal run times of 18 min at 35 °C. Based upon the assumed level of DIP in

Will be conclude that the resolution of these two components would be very good and that any further attempts would only result in lengthy chromatographic runs.

Table 1. NMR Results for Components Analyzed

1. **1,1,1,1-Tetrafluoroethane**

^{19}F

Component	^{19}F Chemical Shift	Area %
$(\text{CF}_3)_2\text{CHF}$	127.1	84.9
$(\text{CF}_3)_2\text{CHF}(\text{OH})$	4.9	2.0
$(\text{CF}_3)_2\text{CHF}(\text{O})$ (TFO)	-1.0	7.2
pyrene	82-72	1.5
oxide, sulfide, pyrene	12-(-30)	4.4

^{13}C

$(\text{CF}_3)_2\text{CHF}$	~28
-----------------------------	-----

^1H

No additional impurities

2. **1,1,1,1-Tetrafluoroethane**

^{19}F & ^{13}C (combined results)

Component	^{19}F Chemical Shift	Mole %
$(\text{CF}_3)_2\text{CHF}$	0.4	85.7
$(\text{CF}_3)_2\text{CHF}(\text{OH})$	20.4	1.0
$(\text{CF}_3)_2\text{CHF}$	0.6	0.0
$(\text{CF}_3)_2\text{CHF}(\text{O})$	4.0	2.4

Table 1. NMR Results for Components Analyzed (Continued)

(RO) ₃ P(O)	0.7	0.7
other	2.4, 1.5, 9.4, 8.8	1.0
From ¹³ C,	2.4, 1.5, 9.4, 8.8	1.0
HOCH ₂ CH(CH ₂ CH ₃)CH ₂ CH ₂ CH ₂ CH ₃		7.6

NOTE: R=CH₃CH₂CH₂CH₂CH(CH₂CH₃)CH₂ - and R'=?

3. DIP:

³¹P, ¹³C, and ¹H (Combined Results):

Compound	³¹ P Chemical Shift	³¹ P Area %	¹³ C Results Mole %
[(CH ₃) ₂ CHO] ₂ P(O)H	5.3	87.7	79.2
(CH ₃) ₂ CHOP(O)(OH)(H)	4.11	11.8	12.1
[(CH ₃) ₂ CHO] ₃ P(O)	-2.5	0.5	0.7
(CH ₃) ₂ CHOH	----	----	8.1

¹H:

A large amount of isopropanol and at least 1 other ³¹P-H compound was observed.

The chromatographic separation analyses involved with using the DB-17 and DB-1701 columns resulted in better separation of the DIP and TIP components. The separations resulting from using the DB-1701 column were superior to those generated by the DB-17 column. The separation on the DB-17 column was adequate; however, the chromatographic peaks returned to pseudo-baseline levels, which returned to true baseline levels after several minutes. In addition, the return to true baseline levels was abrupt, occurring after several minutes. Because of the results achieved with the DB-1701 column, no further developments were attempted.

The DB-1701 column resulted in an appropriate separation of the TIP and DIP components, as well as other impurities within the TIP and BIS matrices. The results are illustrated in Figure 1 and subsequently displayed in Table 2. This was the basis of the initial separation scheme. Figure 2 shows the same programming sequence, which was conducted at a later date; the results are displayed in Table 3. The sample, from which Figure 2 was generated, was exposed to air, thus yielding elevated impurity levels. The peak tailing, observed in Figure 1, was eliminated in Figure 2 by treating the column with solvent flushes of methanol and acetone.

An additional point to note involves the preference for 0.5- μ L injections over those of 1- μ L volumes. One microliter volumes increased the extent of peak tailing. In addition, it should be mentioned that separating TIP from DIP was the major consideration, which is the reason why no further development was initiated to shorten the retention time for the BIS component.

The levels of impurities seen in Figures 1 and 2 are not levels that would be seen regarding the purity specifications required for TIP and BIS. The extent of impurities would reflect a relation to the potential extent of exposure to air, along with other potential degradation sources (e.g., the quantity of water present within each reagent). The identity of 2-propanol and 2-ethyl-1-hexanol were made in correlation with the NMR results. The identity of the 2-ethyl-1-hexanol was not confirmed by an independent sample component injection; however, the extent of molar percentage depicted for 2-ethyl-1-hexanol by NMR results, coupled with the longer retention time tendencies for the BIS related components, tended to imply its location on the chromatogram.

5. CONCLUSION

The results of this investigation indicate that the separation of triisopropyl phosphite (TIP) from bis(2-ethyl-hexyl) hydrogen phosphite (BIS) can be achieved using DB-1, DB-5, DB-1701, and DB-17 columns. The choice of gas chromatographic columns becomes a critical issue when the separation of diisopropyl hydrogen phosphite (DIP) and TIP is considered.

The results of this investigation show that to separate the DIP impurity from the TIP component, a DB-1701 column is recommended for use. The evaluations of DB-1 and DB-5 columns had insufficient separation potential for the DIP and TIP components. Using a DB-17 column provided an adequate separation of the DIP and TIP components; however, the DB-17 column was inferior to the DB-1701 column when peak behavior was analyzed.

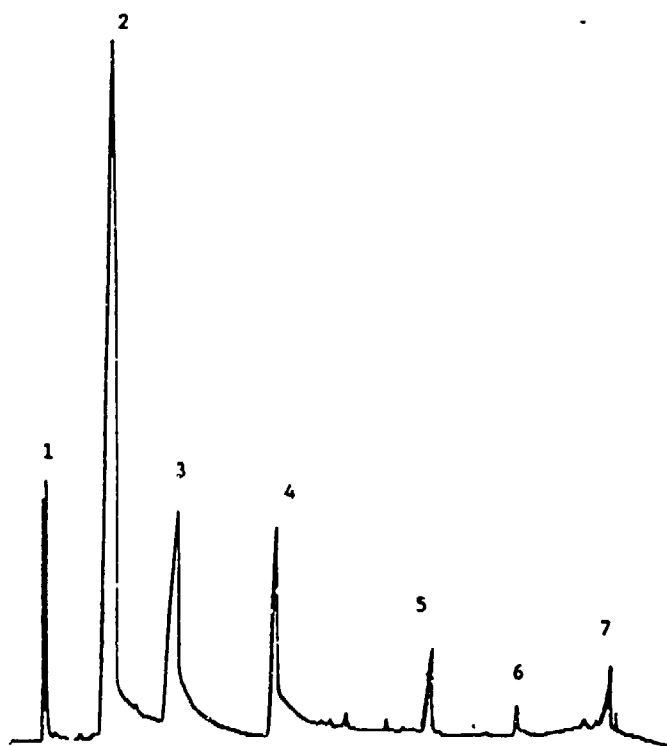


Figure 1. Injection of TIP and BIS

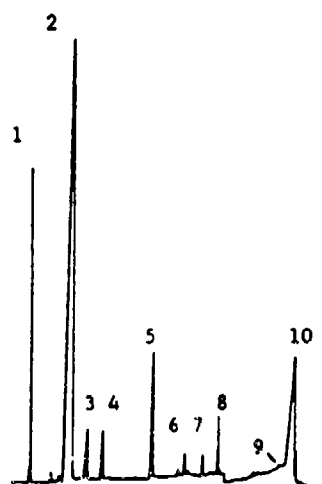


Figure 2. TIP/BIS Injection

Table 2. Results for Figure 1

Component ¹	Retention Time ² (min)	Area ³
1. 2-propanol	1.1	981078
2. TIP	3.44	15685456
3. DIP	5.68	7205570
4. TIPO	8.15	3584104
5. ---	14.63	720318
6. ---	17.63	133136
7. BIS	20.78	831524

¹Some peaks are not listed. In addition, the identification of other major impurities was not investigated.

²Retention times for a helium carrier flow rate of ca. 5 cm³/min using a 30-m megabore, DB-1701 column.

³Area counts corresponding to a total approximate 0.5 μ L volume injection using parameters: TCD (initial range 0.05, attenuation 8), integrator (attenuation 512, peak width 6, chart speed 0.5 cm/min).

Table 3. Results for Figure 2

Component ¹	Retention Time ² (min)	Area ³
1. 2-propanol	1.34	1790
2. TIP	4.17	62417
3. 2-ethyl-1-hexanol ⁴ (BIS impurity)	5.28	3119
4. DIP	6.42	2001
5. TIPO	9.87	5949
6. ---	12.21	507
7. BIS impurity	13.48	454
8. ---	14.55	1854
9. ---	19.2	1594
10. BIS	19.76	17757

¹The identification of all impurities was not investigated.

²Retention times for a helium carrier flow rate of 5 cm³/min using a 30-m megabore, DB-1701 column.

³Area counts corresponding to a total approximate 0.5 μ L volume injection using parameters: TCD (initial range 5.00, attenuation 128), integrator (attenuation 64, peak width 6, chart speed 0.25/cm/min).

⁴The identity of 2-ethyl-1-hexanol was not confirmed but is postulated by the GC and NMR data correlations.